

Solid Solution or Intermetallics in a High-Entropy Alloy

By Yan Ping Wang*, Bang Sheng Li and Heng Zhi Fu

High-entropy alloys, a newly developed alloy system, have attracted much attention for breaking away from the paradigm of designing alloys based on one principal element.^[1–3] High-entropy alloys are defined as those containing at least five principal elements with an atomic concentration between 5% and 35% for each element.^[1] After a period of research, it was soon discovered that their synthesis and processing are feasible and that their properties are excellent.^[4–13]

The as-cast $\text{Al}_x\text{CrFeCoNiCu}$ alloy system has been taken as an example to illustrate the characteristics of high-entropy alloys.^[1] From simple X-ray diffraction (XRD) patterns,^[1] $\text{Al}_x\text{CrFeCoNiCu}$ high-entropy alloys are considered to be solid solution with simple body-centered cubic (bcc) and face-centered cubic (fcc) crystal structure.^[1–3] Furthermore, Yeh et al.^[1–3] proposed the idea that the high mixing entropy of multi-principal-element alloys made random solid solutions more stable than intermetallic compounds. Recently, based on the premise that high-entropy alloys are random solid solutions, the formation rules of solid solution alloys has been proposed.^[14] However, the XRD patterns of high-entropy alloys were just indexed by crystal structure, which means no definite phases have been determined in high-entropy alloys systems. Thus, the conclusion that high-entropy alloys are simple solid solutions needs to be thoroughly tested. Also, the range of applicability of high-entropy idea needs to be tested.^[15]

The CrFeCoNiCu and AlCrFeCoNiCu alloys have typical dendrite microstructures.^[1,11] Also, the dendrite spaces of the two alloys are similar. No phase decomposition has been observed in the dendrite regions of CrFeCoNiCu . Thus, it is reasonable to conclude that CrFeCoNiCu alloy is a solid solution. However, a modulated structure composed of ordered (B2) and disordered (A2) bcc phases has been detected in the dendrite regions of AlCrFeCoNiCu alloy,^[1,11] which implies that phase decomposition occurred in the AlCrFeCoNiCu alloy. Thus, whether AlCrFeCoNiCu alloy is a solid-solution alloy needs further investigation.

A careful phase characterization of AlCrFeCoNiCu alloy, especially to determine if the ordered (B2) phase is a solid solution or intermetallic, is a basic and crucial problem to the high entropy alloys. In this work, the phase constitution in the dendrite regions of AlCrFeCoNiCu high-entropy alloy was reassessed by using selected-area diffraction (SAD) and nanoscale energy dispersive spectrometry (EDS) analyses. As a result, we have found NiAl intermetallics in the AlCrFeCoNiCu alloy. Also, the formation of these NiAl intermetallics greatly influences the mechanical and magnetic properties of the alloy.

Experimental

The AlCrFeCoNiCu (nominal compositions is equimolar) alloy ingots were prepared by a vacuum arc melting the mixtures of pure Al, Cr, Fe, Co, Ni, and Cu with purities of better than 99.9 mass% in a Ti-gettered high-purity argon atmosphere. The ingots were remelted four times to improve homogeneity and then directly solidified in the cold copper hearth. Transmission electron microscopy (TEM) investigations were performed using a FEI Tecnail G20 instrument. A Hitachi S-5500 scanning electron microscope equipped with EDS was used to identify the element distribution of as-cast AlCrFeCoNiCu alloy in nanoscale. Room-temperature compressive properties were tested on an Instron 5500 testing machine with a loading speed of 0.5 mm/min. The test specimens were cylindrical and had dimensions $\Phi 3 \times 5$ mm. Three compression tests were performed to obtain the average value. Magnetic measurements were taken using the physical properties measurement system (PPMS-9, Quantum Design, Inc) in an applied field up to 5 T.

Results and Discussion

The XRD and SEM microstructure of prepared AlCrFeCoNiCu alloy was presented in our report.^[16] Figure 1a shows the TEM bright-field image of the dendrite regions in the AlCrFeCoNiCu alloy. It can be seen that the dendrite regions present a modulated structure, which are labeled β zone and β' zone, respectively. The β zone is about 30 nm and the β' zone is about 50 nm wide. It is also can be seen that some nanoparticles are precipitated in the β' zone. The precipitates were found to have a face-centered orthorhombic structure ($a = 0.6$ nm, $b = 0.52$ nm, $c = 0.71$ nm).^[11]

The modulated structure present here are consistent with that reported by Yeh et al.^[1] As reported,^[1,11] the modulated structures are composed of ordered (B2) and disordered (A2) bcc phases. Thus, it is necessary to distinguish bcc disordered

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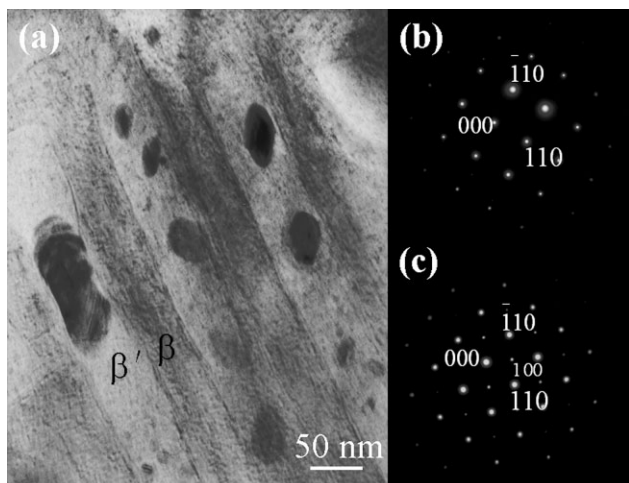


Fig. 1. Bright-field TEM image and SADPs of the dendrite region of AlCrFeCoNiCu alloy. (a) Bright-field TEM image; (b) SADP of β along the [001] zone axis; (c) SADP of β' along the [001] zone axis.

phase (A2) from bcc ordered phases (B2). From the SAD results, it can be seen that the β zone is the bcc disordered phase (Fig. 1b), while the β' zone is the bcc ordered (B2) phase (Fig. 1c).

In this research, we applied a Hitachi S-5500 scanning electron microscope to identify the distribution of elements in nanoscale. From the results of EDS line-scanning analysis (Fig. 2), it can be seen that the β phase is enriched with Cr and

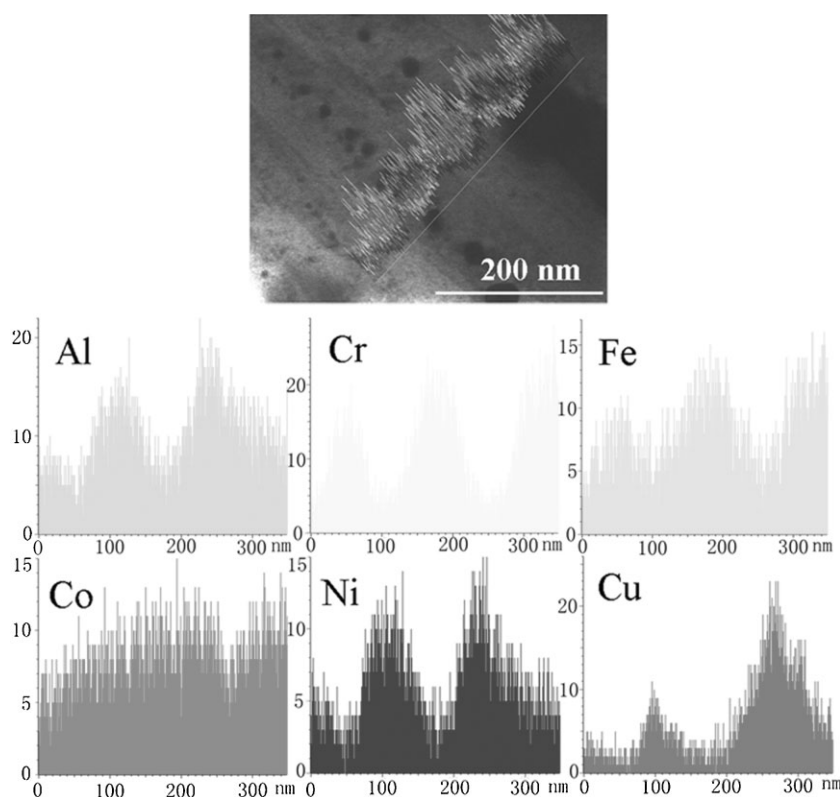


Fig. 2. EDS line scanning analysis of AlCrFeCoNiCu alloy.

Fe, while the β' phase is enriched with Ni and Al. The distribution of Co is relatively uniform. The precipitates within the β' phase are rich in Cu.

There is no Fe, Cr, or Co ternary phase in the ICDD database. In the Fe, Cr, and Co ternary phase diagram, the existing bcc phases are α -Fe, α -Cr, and (α -Fe, Cr) solid solutions.^[17] By considering the phase composition, β phase can be identified as a (α -Fe, Cr) solid solution. The β' -ordered bcc phase consists mainly of Al and Ni elements along with a certain amount of Co. The crystal structures of Al and Ni are both fcc. Co has a hexagonal close-packed (hcp) crystal structure and an fcc crystal structure at high temperature. The β' phase has an ordered bcc crystal structure that differs from those of each of the main components, but the same crystal structure as NiAl intermetallics. Considering that Co has high solubility in NiAl intermetallics,^[18] the β' phase is determined to be a NiAl intermetallic based phase.

It can be concluded that the modulated structure of the AlCrFeCoNiCu alloy consist of a (α -Fe, Cr) solid solution (A2) and a NiAl intermetallic phase (B2). Also, some Cu-enriched face-centered orthorhombic phase precipitates in the NiAl intermetallics. The ordered bcc phase was also detected in AlSiTiCrFeCoNiMo_{0.5} and AlSiTiCrFeNiMo_{0.5} alloys.^[4] Thus, the scope of applicability of the high-entropy theory in other multi-principal-element alloys needs to be addressed in further studies.

Yeh et al.^[1] have pointed out that the high-entropy idea does not apply to materials with very large heats of formation, such as oxides, carbides, and borides. Moreover, we have found that Al and Ni atoms form an intermetallic phase when Al is added into the CrFeCoNiCu system in an equimolar ratio. It is apparent that Al has a much larger atomic radius (1.4317 Å) than the other elements and strong binding force with the other elements.^[1] The addition of Al tends to make the solid solution unstable. Among all the atom pairs, Al and Ni has the maximum negative mixing enthalpy, indicating the strongest compound forming tendency between Ni and Al atoms. As the results show, even in a senary alloy, Al and Ni atoms can form NiAl intermetallic compound. Since ordering in conjunction with spinodal decomposition has been reported in many alloy systems containing Al,^[19–21] it is suggested that there is a more complicated ordering and spinodal decomposition process.

From a thermodynamic viewpoint, the formation of a random solid solution or an intermetallic phase depends on the competition of entropy and enthalpy. The random solid-solution state possesses the maximum mixing entropy, while the formation of intermetallics will release high formation enthalpy. Evidently, in the AlCrFeCoNiCu

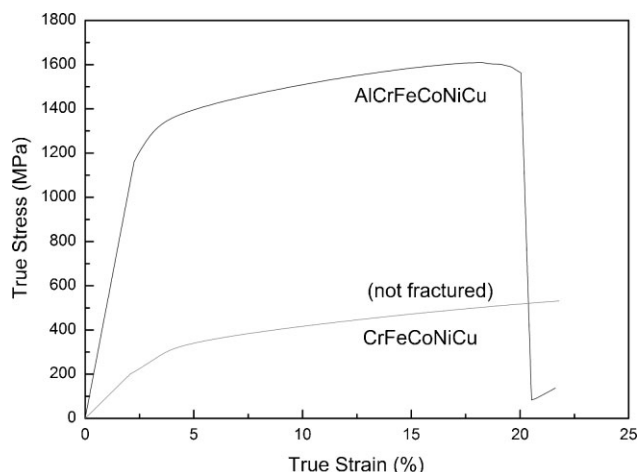


Fig. 3. True stress–true strain curves of AlCrFeCoNiCu and CrFeCoNiCu alloys under compression.

alloy, the mixing entropy is not sufficient to overcome the contribution of formation enthalpy to the decrease of Gibbs free energy.

Figure 3 shows the true stress–true strain curves of AlCrFeCoNiCu and CrFeCoNiCu alloys under compression at room temperature. On adding an equimolar ratio of Al to the alloy, the yield stress of the AlCrFeCoNiCu alloy reaches 1147 MPa, which is much higher than that of CrFeCoNiCu alloy (237 MPa). As described in the introduction, the main difference between the two alloys is the structure of dendrite regions. Thus, the great difference of properties is caused by the phase decomposition of AlCrFeCoNiCu alloy. AlCrFeCoNiCu alloy was considered in the literature^[1] to be a solid solution. This great difference was interpreted as the solution hardening mechanism of larger atomic radius element Al.^[1] However, from the above analysis, Al is not acting as a solution element. The addition of Al forms a NiAl intermetallic phase, which is a high-strength phase. Moreover, the

combination of NiAl intermetallics, (α -Fe, Cr) solid solution, and Cu enriched phases constitutes the multiphase strengthening.

Figure 4 illustrates the initial magnetizations measured in an applied field of 5 T. The CrFeCoNiCu alloy shows typical paramagnetic behavior. The magnetization of the AlCrFeCoNiCu alloy presents typical ferromagnetic behavior. The AlCrFeCoNiCu alloy approaches saturation at approximately 40 emu/g. It can be seen that the phase decomposition change the alloy from typical paramagnetic behavior to typical ferromagnetic behavior. The NiAl intermetallic is weak magnetic phase and the (α -Fe, Cr) solid solution is magnetic phase. In addition, the weak magnetic phase and magnetic phases constitute the modulated structure, which is similar to some hard magnetic alloys, such as AlNiCo and FeCoNi.^[22,23]

Conclusion

In summary, NiAl intermetallic phases have been identified in AlCrFeCoNiCu alloy, indicating that the mixing entropy is not sufficient to inhibit the Al and Ni atoms from forming intermetallics in this alloy system. The main causes of strengthening are the formation of NiAl intermetallics. Also, the AlCrFeCoNiCu alloy displays typical ferromagnetic behavior because of the decomposition of paramagnetic NiAl intermetallics and a magnetic (α -Fe, Cr) solid solution. Thus, the high-entropy idea does not apply to the AlCrFeCoNiCu alloy. Also, the existing research conclusions that are proposed on the premise that high-entropy alloys are random solid solutions need to be re-investigated.

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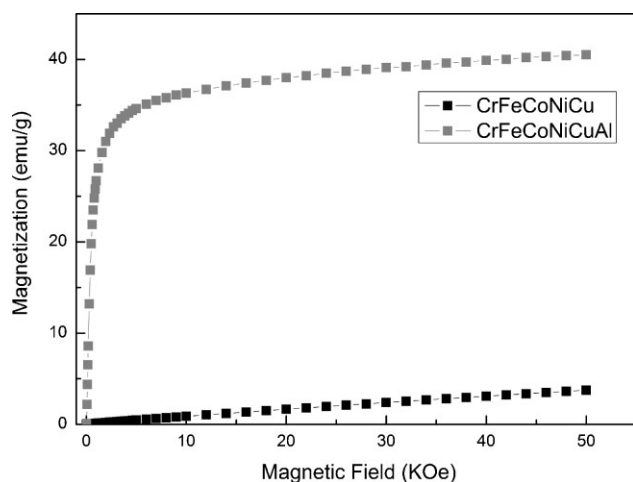
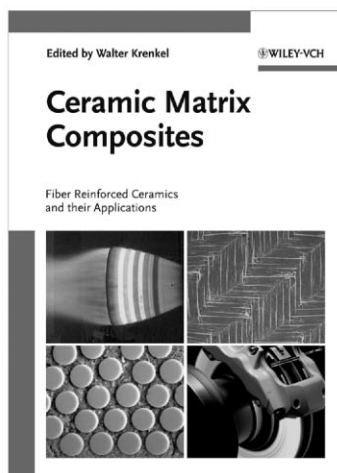


Fig. 4. Magnetization curves of AlCrFeCoNiCu and CrFeCoNiCu alloys at room temperature.

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